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Ambient Ammonia Measurements in Coastal Southeastern Virginia

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16. ABSTRACT

The first systematic set of in-situ measurements of ambient ammonia have been made on the U.S. East Coast. These measurements show that the ammonia concentration during the measurement period, while highly variable (ranging from .2 to 5 ppbV) are on the low end of the range published for non East Coast sites. The time averaged ammonia levels obtained at the Langley Research Center and Great Dismal Swamp sites are comparable in magnitude; however, significant differences were found when individual samples taken at the two sites at approximately the same time were compared. In addition to the spatial variation, a strong random temporal variation was observed. Correlations were found between the ammonia concentration and certain meteorological parameters, i.e., wind direction and rainfall. Ammonia concentrations were lower in air masses arriving from over water (1.8 ppb) than over land (2.3 ppb). During periods of rain the ammonia measurements were lower, 1.3 ppb compared to 2.2 ppb during other periods. In addition, a seasonal change was also noted, i.e., the NH_3 concentrations decreased from 2-3 ppbV in late summer to < 0.2 ppbV in the early winter.

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AMBIENT AMMONIA MEASUREMENTS IN COASTAL SOUTHEASTERN VIRGINIA

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Abstract— Results are presented from a measurement program to test an *in situ* ammonia measurement technique and to document the temporal and spatial variability associated with ammonia. The ammonia data were accumulated for two sites in coastal Southeastern Virginia from 15 Aug. 1979 to 31 Dec. 1979.

INTRODUCTION

Measurements of ambient ammonia show that its atmospheric mixing ratio varies from < 0.1 ppbv to several tens of ppbv (e.g. Breeding *et al.*, 1973; Breeding *et al.*, 1976; Lodge *et al.*, 1974) near ground level and that NH_3 concentration decreases monotonically with altitude (Georgii and Muller, 1974; Hoell *et al.*, 1982) implying a distributed ground level source. Ammonia is the most abundant basic gas (Lau *et al.*, 1977) and as such it plays a significant role in atmospheric chemistry in neutralizing acid sulfate and nitric acid (Brosset, 1978; Tang, 1980). For example, field studies in Sweden (Brosset *et al.*, 1975) have shown that the effects of acid rain are mediated by the presence of NH_3. In general, however, the lack of sensitive and specific analytical techniques has limited the number of atmospheric measurements of ammonia. This paper presents results from a measurement program to test ammonia measurement techniques and to document the temporal and spatial variability associated with ammonia. The ambient ammonia data were accumulated for sites in coastal Southeastern Virginia from 15 Aug. 1979 to 31 Dec. 1979.

MEASUREMENT TECHNIQUE

The *in situ* monitoring technique utilized in this study involves short term integrative sampling onto Teflon beads with subsequent analysis by photoacoustic detection of the desorbed ammonia (McClenny and Bennett, 1980). Calibrated NH_3 loadings were obtained by sampling ammoniated air from the output of the permeation system for given time periods. The calibration data consisted of response values for 57 68 ng loadings, 14 34 ng loadings and 13 13.6 ng loadings. A linear least-squares fit to the data resulted in the calibration relation $R = 0.65L + 0.33$ where R is the system response and L is the amount of NH_3 in ng. The small positive offset is probably due to an accumulation of NH_3 on the collection tube and/or transfer lines. The precision of the calibration was characterized by a standard deviation of 10% for the 68 ng and 34 ng loadings; and of 20% for the 13 ng loadings. At 290 °C and 760 Torr and taking a 20 min sample at 1 ℓ min^{-1} sampling rate, these measures of precision correspond to an uncertainty of 0.48 ppbv at the 4.82 ppbv level, 0.24 ppbv at the 2.41 ppbv level and 0.18 ppbv at the 0.92 ppbv level. The limited precision was apparently due to the effect of small and variable amounts of NH_3 adsorbed on the collection medium during handling and to residual ammonia in the Chromosorb T itself.

Tests have been performed with both humidified and dry calibration air to demonstrate that the relative humidity has negligible effect on the system's response to NH_3. Additional checks for interference from unknown atmospheric absorbers were made by simultaneously drawing two ambient samples and analyzing with different laser emission lines, the $R(18)$ line in the $(00^{0}1\text{–}10^{0}0)$ transition for $^{13}C^{16}O_2$ and the $R(30)$ line in the $(00^{0}1\text{–}02^{0}0)$ transition for $^{12}O^{16}O_2$. The simultaneous samples analyzed in this manner agreed within experimental uncertainty. Some interference from dimethylamine and trimethylamine has been previously noted (McClenny and Bennett, 1980). During this study only a few ambient samples indicated the presence of the broad underlying response curve characteristic to these amines and these were not included in the data.

In-line particle filters are used, as in past studies (McClenny and Bennett, 1980) to prevent ammonium-containing particles from being collected on the Teflon bead trap where ammonia could subsequently be released during heating. The filter can be the source of interferences if there is a net gas-to-particle or particle-to-gas conversion occurring at the filter surface or if the filter itself releases or absorbs NH_3. Our own experience has shown that new particulate filters can release or absorb NH_3 during initial use and require "conditioning" or exposure to ambient air for one sampling period (20 min)

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Table 1. Side-side-outdoor runs for NH_3 (in $ng\ell^{-1}$)

	Time 9:28	9:55	10:45	11:16	11:38	12:07	12:33	1:03	1:32
Teflon beads	0.92	0.75	0.96	0.72	0.83	0.98	0.67	1.03	0.77
Diffusion tubes	1.01	1.17	0.80	1.02	1.93	1.00	0.93	0.68	0.94

Average Teflon = $0.85\ ng\ell^{-1}$; average diffusion = $1.05\ ng\ell^{-1}$.

before reliable data can be obtained. Changing the filter with every sample minimizes net conversions due to contact between non-fractionated particles (Ferm, 1979) while short sampling time reduces the likelihood of changes in atmospheric equilibrium during sampling (Shaw *et al.*, 1981).

Subsequent to the measurements described here, a new, short-term sampling technique was developed which requires no in-line filter (Braman *et al.*, 1982, and McClenny *et al.* 1982). This technique is based on the separation of particles and gases by their different rates of diffusion to the walls of a hollow, coated tube through which the sample passes. We are now collecting data using this technique. A limited number of comparisons between the two techniques were made on the Langley Research Center grounds on 12 April 1980 and are shown in Table 1. The average of results obtained with the Teflon bead trap was $0.85 \pm 0.14\ ng\ell^{-1}$; omitting the anomalously high diffusion tube results at 11:30, its average was $0.94 \pm 0.15\ ng\ell^{-1}$.

RESULTS

Table 2 lists the experimental values obtained at two locations in Southeastern Virginia from 16 August 1979 to 19 September 1979. The first of these sites was at the Langley Research Center (LaRC) (37° 5′ N latitude, 76° 21′ W longitude) in Hampton, VA. The other was at the Naval Communication Center (36° 34′ N latitude, 76° 11′ W longitude) in Chesapeake, VA. This later site was bordered on the west by the Great Dismal Swamp (GDS). These two sites were chosen because of their somewhat different character; the LaRC site represents an urban type environment and GDS a rural environment. The maximum and minimum NH_3 concentrations at GDS were 4.0 ppbv and 1.5 ppbv, respectively. At LaRC, these concentrations were, respectively, 4.0 and 0.2 ppbv. The average NH_3 concentration, at the GDS was 2.7 $\pm$ 0.2 ppbv for 24 measurements and at the LaRC was 2.0 ± 0.1 ppbv for 55 measurements. Individual GDS concentrations were found to be roughly twice that obtained at the LaRC site for samples obtained when sampling at approximately the same time. Figure 1 shows the average daily concentrations taken during the period included in Table 2 as well as several additional measurements taken during the late fall and early winter at the LaRC site. We believe the decrease in concentration during October was due to lower biogenic activity associated with the reduced soil temperature (Dawson *et al.*, 1977). The value of the NH_3 concentration which we measured during this later period should be considered as an upper limit because of the sensitivity limit of our method.

The data show strong variations in NH_3 concentrations between consecutive samples at the same site with the concentration changing, at times, by a factor of two. Variations inherent in the technique do not explain this since the average of ratios of difference to sum of 19 paired samples has been measured as only 10.2%. This type of variability has also been noted by others (Abbas and Tanner, 1981; Appel *et al.*, 1978; Bos, 1980) and indicate the strong influence localized natural and/or anthropogenic sources can have on *in situ* NH_3 measurements.

The data also suggest that the average NH_3 level is dependent upon the wind direction with the lowest concentrations for our site being associated with flow from the easterly direction. The average concentrations for wind flow from the east, north, south and west during the time covered by measurements shown in Table 2 were 1.6 ± 0.1 ppbv (31 samples), 3.1 ± 0.6 ppbv (4 samples), 2.5 ± 0.2 ppbv (8 samples) and

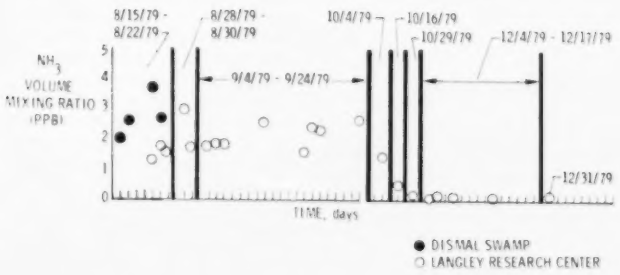

Fig. 1. The seasonal variation of ground level ammonia.

Table 2. Ammonia concentrations in southeastern Virginia from 16 August to September 1979

Date	Time (EDT)	Concentration (ppbV) LaRC	GDS	Date	Time (EDT)	Concentration ppbV LaRC	GDS
16 Aug. 1979	13:23		2.17	8/22/79	14:02	.97	
	13:23		1.72		14:25	1.05	
	13:44		1.49		15:09	1.12	
	13:44		1.57		15:31	1.57	
	14:05		1.53		16:03	2.61	
	14:05		1.53		17:42	2.60	
	15:24		2.44		21:00	1.62	
	18:03		2.33		22:39	.97	
	18:42		3.13	8/29/79	13:45	3.18	
	23:39		2.15		14:15	2.84	
17 Aug. 1979	1:18		2.76	8/30/79	10:49	1.94	
20 Aug. 1979	12:35	1.27			11:17	1.72	
	13:13	1.42			12:00	3.06	
	13:53		3.44		12:30	1.05	
	14:15	1.72			12:59	1.34	
	15:01	.75			13:25	1.57	
	15:32		3.29		15:12	.97	
	17:11		4.95	9/5/79	11:35	2.09	
	20:29		4.71		13:35	1.42	
	22:08		3.00		14:54	1.65	
	23:47		3:00	9/6/79	11:38	1.06	
21 Aug. 1979	5:31		2.24		12:00	2.64	
	7:10		2.31	9/7/79	12:30	2.54	
	8:49		3.24		14:10	2.04	
	10:20	2.24			14:31	1.61	
	10:28		3.44		15:03	1.19	
	10:41	1.49		9/11/79	9:58	.50*	
	11:04	1.79			11:07	.22*	
	11:50	1.57		9/12/79	12:05	3.64	
	12:07		2.49		12:21	4.02	
	12:12	2.02			12:52	3.03	
	13:40	1.49			14:20	3.23	
	13:46		2.46		14:42	1.89	
	14:02	1.42		9/17/79	16:16	1.55	
	14:34	1.79		9/18/79	8:30	2.53	
	14:56	1.79			9:02	3.13	
	15:17	2.2			10:11	.98*	
	15:25		3.01		12:15	3.19	
	16:03	1.54			15:29	2.23	
				9/19/79	10:07	3.21	
					10:27	1.50	
					10:54	2.27	

* These data points were taken from air parcels originating from the direction of a local steam generating plant.

2.1 ± 0.2 ppbv, respectively. The data used to obtain the average concentrations were restricted to that obtained from the LaRC site and for average wind speeds greater than 5 knots. While the difference between the NH_3 measured during winds from the north, south and west is relatively small, the average concentration measured for an easterly wind is clearly lower. With an easterly wind, the air mass being sampled is influenced by the presence of the Atlantic ocean, implying a lower production of NH_3 in the ocean than on land. For the measurement period covered in Table 2, winds from the east were typically sustained for only 12 to 24 h. Consequently, the lower levels we have observed are probably characteristic of mixed land and marine air masses and would indicate an NH_3 concentration over the ocean of less than 1.6 ppbv.

We have also noted a decrease in the average NH_3 level for samples obtained during and immediately after (within 15 min) periods of rain. The average NH_3 concentration over several days when it was raining was 1.3 ± 0.4 ppbv while on the clear days, during the observation period, the average concentration was 2.2 ± 0.3 ppbv. This decrease is consistent with previous observations (McClenny and Bennett, 1980). The scavenging of NH_3 at ground level might be the consequence of droplet formation in a region of lower NH_3 concentration and a subsequent net exchange of NH_3 between the droplet and the gaseous NH_3 at ground level in the approach to a new equilibrium.

This possibility is consistent with the equilibrium conditions predicted by Tang (1980) and by Lau and Charlson (1977). These treatments also imply that the NH_3 concentration typical of the summer months could only be consistent, under conditions of equilibrium, with a sulfate aerosol for which the molar ratio of ammonium to sulfate is high, i.e. ammonium sulfate is more likely than ammonium bisulfate. Additional experiments are needed to verify this implication.

CONCLUSIONS

We have presented a systematic set of *in situ* measurements of ambient NH_3 at two sites on the U.S. East Coast. These measurements show that the NH_3 concentration during the measurement period, while highly variable (ranging from 0.2 to 5 ppbv), are on the low end of the range published for non East Coast sites. The time averaged NH_3 levels obtained at the Langley Research Center and Great Dismal Swamp sites are comparable in magnitude; however, significant differences were found when individual samples taken at the two sites at approximately the same time were compared. In addition to the spatial variation, a strong random temporal variation was observed. Correlations were found or implied between the NH_3 concentration and certain meteorological parameters, i.e. wind direction and rainfall. The average NH_3 concentration was lower in air masses arriving from over water (1.6 ppb) than over land (3.1 ppb). During periods of rain the average NH_3 concentration was lower, 1.3 ppb compared to 2.2 ppb during other periods. In addition, a seasonal change was also noted, i.e. the NH_3 concentrations decreased from 2–3 ppbv in late summer to < 0.2 ppbv in the early winter.

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